

# Effect of Adjuvants on the Therapeutic Activity of Dimethomorph in Controlling Vine Downy Mildew. I. Survey of Adjuvant Types

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**Abstract:** The effect of adjuvants on the performance of emulsifiable concentrate (EC) and wettable powder (WP) formulations of dimethomorph, a new systemic Oomycete fungicide, has been investigated using a two-day therapeutic (curative) assay with downy mildew (*Plasmopara viticola*, Berl. & de T.) on vines (*Vitis vinifera* L., cv. Cabernet Sauvignon) in glasshouse trials.

The EC formulation had some therapeutic activity in this type of test. This activity was increased by the spray tank incorporation of 6 g litre<sup>-1</sup> of either emulsifiable rape seed oil ('Atplus' 412) or emulsifiable paraffinic oil ('Atplus' 411F). However, these improvements in performance were overshadowed by those brought about by incorporation of 3 g litre<sup>-1</sup> of a series of C<sub>13</sub>/C<sub>14</sub> alcohol ethoxylates varying in ethylene oxide content from 5 to 20 moles: ('Marlipal' 34/6EO, 34/11EO, 34/20EO). Nearly complete fungal control was obtained in the presence of these adjuvants with a dimethomorph application rate of 25 g ha<sup>-1</sup> compared with only around 90% control at 400 g ha<sup>-1</sup> without adjuvants.

The WP formulation was inactive in this therapeutic test but the presence of the adjuvants improved the performance of this formulation towards the high levels observed with the EC plus adjuvants, demonstrating that adjuvants could markedly influence the performance of solid, otherwise therapeutically inactive, dimethomorph formulations.

Further trials examined other types of adjuvants (nonylphenol, alkylamine and silicone ethoxylates) but either they were no better than the alcohol ethoxylates or they induced unacceptable phytotoxicity. Trials with alcohol ethoxylates ('Genapols') from another source demonstrated activity equivalent to the 'Marlipal' surfactants. A two-factorial matrix experiment with 'Genapol' C050 showed that, under glasshouse conditions, >90% control could be obtained with the dimethomorph EC at 25 g AI ha<sup>-1</sup> with 375 g ha<sup>-1</sup> 'Genapol' C050. Applications of the WP formulation required slightly higher rates of either 50 g AI ha<sup>-1</sup> plus 375 g ha<sup>-1</sup> 'Genapol' C050 or 25 g AI ha<sup>-1</sup> plus 750–1500 g ha<sup>-1</sup> 'Genapol' C050.

The overall conclusion was that alcohol ethoxylates varying in alkyl chain length from C<sub>12</sub> to C<sub>18</sub> and ethylene oxide content between 5 and 20 moles for the C<sub>12</sub> surfactants and ~15 moles for the C<sub>18</sub> surfactants were effective adjuvants in promoting the therapeutic activity of dimethomorph formulations against *P. viticola* on glasshouse-propagated vines.

**Key words:** fungicide, dimethomorph, vine, *Vitis vinifera*, downy mildew, *Plasmopara viticola*, adjuvants, formulation.

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## 1 INTRODUCTION

Dimethomorph ((*E,Z*)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloyl]morpholine,  $\text{Log } K_{ow} = 2.7$ ) is a new systemic Oomycete fungicide, with a novel mode of action, being commercialised for the control of downy mildew (*Plasmopara viticola* Berl. & de T.) on vines (*Vitis vinifera* L.) and late blight (*Phytophthora infestans* de Bary) on potatoes (*Solanum tuberosum* L.) and tomatoes (*Solanum lycopersicum* L.), and on other crops.<sup>1-5</sup> While studies have shown that it possesses translaminar activity<sup>1,3</sup> and is systemic via either root uptake<sup>1</sup> or leaf to leaf (stem to leaf) transfer,<sup>3</sup> the main initial uses will be as a protectant fungicide with some curative (therapeutic) activity and excellent anti-sporulant activity with long residual protection.

Protectant action may be derived from the action of residues of spray applications on leaf surfaces, but therapeutic action can only be derived from active ingredient that has penetrated in sufficient concentration into foliar tissue and inhibited any further development of fungal infection in that tissue. This element of penetration could not only be important in destroying any early stages of infection, thereby broadening commercial use, but could also provide the possibility of reducing application rates and, furthermore, could impart a measure of rainfastness, since the penetrated active ingredient would not be subject to physical removal by rain.

Adjuvants (emulsifiable oils, surfactants, etc.) can influence both the spray deposition and the foliar penetration processes of crop protection chemicals which, in turn, can affect their biological performance. Indeed, preliminary studies with different types of dimethomorph formulation containing different amounts of surfactants showed that different levels of activity could be obtained in glasshouse tests against both *P. viticola* on vines and *P. infestans* on tomatoes (C. L. Dunn, pers. comm.). Thus there was circumstantial evidence that dimethomorph could be induced to penetrate leaf cuticles. It seemed that a systematic investigation of the effect of different types of adjuvant on the performance of dimethomorph was warranted to see whether any or all of the possible benefits mentioned above could be achieved.

It was decided, in the first instance, to utilise a fungicidal screen involving vines and the disease, *P. viticola*, in a therapeutic assay of a two-day-old infection. The reasons were that the disease was inoculated and the symptoms subsequently expressed only on the abaxial leaf surface. The propagation of the plants ensured that, at the time of application, two days after inoculation, the leaves were horizontal and that spray was applied only to the adaxial surface. Any expression of fungicidal activity could, therefore, only arise by permeation of dimethomorph into the cellular tissue. Since vine leaves have an easily wet surface, spray deposition is unaf-

ected by changes in spray solution surface tension,<sup>6</sup> as mediated by adjuvants, and thus the assay focused attention on the ability of adjuvants to promote the foliar penetration of dimethomorph. This paper reports on some of the first glasshouse experiments.

## 2 EXPERIMENTAL

### 2.1 Materials

Formulations of dimethomorph were prepared by the Formulation Department at either Sittingbourne Research Centre or Shell Forschung, Schwabenheim to the following general recipes: emulsifiable concentrate (EC), dimethomorph, 100 g; emulsifiers, 80 g; mixed solvents to 1 litre; wettable powder (WP), dimethomorph, 500 g; dispersing agents, 100 g; inert filler, 400 g.

Adjuvants were obtained as follows: 'Atplus' 411F, 412, ICI Specialty Chemicals, Kortenberg, Belgium; 'Marlipal' 34/6EO, 34/11EO, 34/20EO ( $C_{13}/C_{14}$  alcohol ethoxylates with 6, 11, 20 moles of ethylene oxide) Huls AG, Marl, Germany; 'Arkopal' N060, N100, N230 (nonylphenol ethoxylates with 6, 10, 23 moles of ethylene oxide), 'Genapol' C050, C080 ( $C_{12}$  alcohol ethoxylates with 5, 8 moles of ethylene oxide), 'Genapol' T110, T150, T250, T800 ( $C_{16}/C_{18}$  alcohol ethoxylates with 11, 15, 25, 80 moles of ethylene oxide), 'Genamin' C020, C050, C100, C200 ( $C_{12}$  alkylamine ethoxylates with 2, 5, 10, 20 moles of ethylene oxide), 'Emulsogen' EL, EL400 (castor oil ethoxylates with 36, 40 moles of ethylene oxide) were obtained from Hoechst AG, Frankfurt, Germany; 'Silwet' L77 (dimethylpolysiloxane ethoxylate/propoxylate), Union Carbide, Banbury, USA; 'Ethomeen' C12 (alkylamine ethoxylate with 12 moles of ethylene oxide), Akzo, Amersfoort, The Netherlands.

### 2.2 Plants and inoculation procedure

Vine plants (*V. vinifera*, cv. Cabernet Sauvignon) were propagated from woody cuttings and grown to the five- to six-leaf stage under glasshouse conditions (temperature, 22°C day, 17°C night; illumination, natural daylight supplemented by mercury vapour lighting, 100  $\mu\text{mole m}^{-2} \text{s}^{-1}$ , to give a 16-h photoperiod; relative humidity, 65–80%; watering by sub-irrigation of a dilute solution of balanced fertilisers). The apex and top immature leaf of each plant were removed before inoculation of the abaxial surface of the expanded top two leaves by spraying with a freshly prepared suspension of *P. viticola* (60 000 spores  $\text{ml}^{-1}$ ) in water obtained from previously infected plants. After inoculation the plants were transferred to a high humid-

ity chamber (relative humidity, 95–100%) for 20 h and then returned to the glasshouse for a further 24 h before spray treatment.

### 2.3 Preparation and application of spray solutions

The general procedure was to prepare dispersions of the dimethomorph formulations and adjuvants, separately, at double the concentrations required for application. Immediately prior to spraying, equal volumes of the dimethomorph formulation and adjuvant dispersions were mixed. For example, for the results in Tables 1 and 2, aliquots (8, 4, 2, 1, 0.5 ml) of the EC formulation and amounts (1.6, 0.8, 0.4, 0.2, 0.1 g) of the WP formulation were dispersed in tap water (250 ml). An appropriate amount of adjuvant (emulsifiable oil, 3 g; surfactants, 1.5 g) was dispersed in tap water (250 ml). A volume (20 ml) of each dimethomorph formulation dispersion was mixed with an equal volume of the appropriate adjuvant dispersion. Each of these mixed dispersions was sprayed onto four vine plants using a laboratory track sprayer equipped with a 800067 hydraulic flat fan nozzle (Spraying Systems Co., Illinois) operating at 276 kPa to give a volume rate equivalent to 250 litre ha<sup>-1</sup>.

At this volume rate, dimethomorph and adjuvants were applied at the rates given in Tables 1 and 2. In succeeding trials, concentrations of dimethomorph formulations and adjuvants were adjusted appropriately. In all trials four inoculated plants were sprayed either with water, to act as untreated controls, or with diluted adjuvant solution containing no dimethomorph.

### 2.4 Plant treatment and assessment

The spray deposits were allowed to dry and the plants returned to the glasshouse conditions, described above, and placed in a randomised block on the glasshouse bench for four days. They were then transferred to a high humidity room (relative humidity, 95–100%) for 24 h, incorporating a dark period of 8 h, to induce sporulation. Each inoculated leaf was assayed for extent of infection by visual estimation of the percentage area of leaf covered by sporulating lesions. The mean value of the eight estimates (four plants, two leaves per plant) for each treatment was converted into percentage fungal control by the equation

$$\% \text{ control} = 100[(A - B)/A] \quad (1)$$

where  $A$  = area of infection (%) on leaves sprayed with water

$B$  = area of infection (%) on treated leaves.

and the results given in the tables. The area of infection on the leaves sprayed only with water varied between 0

and 100% in any one trial and varied between trials. The mean values were generally in the range 40–60% but could be as high as 90%.

Statistical analysis of differences between treatments was conducted by either of two methods:

(1) The first two trials were analysed by comparing the percentage infection for each treatment with the infection on untreated plants, assuming a binomial type error with a heterogeneity factor, using the mean score of the two leaves on each plant as a replicate. The estimate of this difference, and its standard error, was measured on the logistic scale:

$$D = \log[(I_t - I_c/20)/100 - (I_t - I_c/20)]$$

where  $I_t$  = estimated infection for each treatment,  $I_c$  = estimated infection for untreated plants and  $D$  = difference between treated and untreated plants. A one-sided  $t$ -test of whether this difference exceeded zero was performed, at a 5% significance level, using the generalised linear modelling programme in Genstat IV. In this way it was possible to identify those treatments which failed to reduce infections by at least 95% at a 5% significance level. In the tables the remainder of the results are given in bold type. Since the test was applied repeatedly, there was an increased risk of a false positive identification but these should be eliminated in any subsequent testing.

(2) The remaining trials were analysed by Student's  $t$ -test on the percentage fungal control values obtained from eqn (1), assuming normal distribution, to identify those treatments that gave >90% control at  $P = 0.05$ .

## 3 RESULTS AND DISCUSSION

It was observed from all the tests in this work that for those plants sprayed only with water, or with treatments that gave little or no control of a two-day-old infection of *P. viticola* on vines, the extent of variation between replicates was high (coefficients of variation up to 100%). This was because of innate variation in the infectability of the vine leaves. It is a well-known phenomenon in this type of work and has no simple solution to the problem (C.L. Dunn, pers. comm.). The consequence is that this variation limited the ability to detect significant differences between treatments. Furthermore, the nature of the results usually prevented construction of dose response curves and hence calculation of concentrations for specific levels of control. Statistical analysis was therefore conducted using comparisons between treated plants and those sprayed with water or adjuvant solution and  $t$ -tests. No fungicidal effect of any adjuvant solution was detected.

Despite the variability, a reasonable dose response trend of increasing therapeutic control of *P. viticola* was

**TABLE 1**  
Effect of Adjuvants on the Therapeutic Control of Two-Day-Old Infections of *Plasmopara viticola* on Vine by Dimethomorph Formulations

Adjuvant		Fungal control (%) <sup>a</sup>					Mean <sup>b</sup>
Type	Application rate (g ha <sup>-1</sup> )	Dimethomorph application rate (g ha <sup>-1</sup> )					
		25	50	100	200	400	
(a) EC formulation							
None	—	10	17	74	70	92	53
'Atplus' 412	1500	51	77	78	89	97	78
'Atplus' 411F	1500	89	91	69	90	95	87
'Marlipal' 34/6EO	750	100	100	100	100	100	100
'Marlipal' 34/11EO	750	99	98	98	100	100	99
'Marlipal' 34/20EO	750	100	98	97	100	100	99
(b) WP formulation							
None	—	0	0	0	0	0	0
'Atplus' 412	1500	25	50	54	39	34	40
'Atplus' 411F	1500	75	75	32	27	18	45
'Marlipal' 34/6EO	750	98	98	100	100	100	99
'Marlipal' 34/11EO	750	98	96	96	98	100	98
'Marlipal' 34/20EO	750	95	100	100	98	96	98

<sup>a</sup> Figures in bold type are those identified as not less than 95% control at  $P = 0.05$  by the statistical method 1.

<sup>b</sup> Mean values of fungal control through the dimethomorph application rate range: these facilitate comparison of the adjuvant treatments.

observed with increasing application rate of the EC formulation (Table 1(a), with >90% control at a dimethomorph application rate of 400 g ha<sup>-1</sup>. Incorporation of the emulsified rape seed oil, 'Atplus' 412, gave improved levels of disease control at all application rates of dimethomorph, approaching 90% at 200 g ha<sup>-1</sup>, and represented a reasonable improvement (Table 1(a)). Similar improvements, possibly marginally better at low dimethomorph application rates, were obtained with the emulsifiable paraffinic oil, 'Atplus' 411F, but these were overshadowed by the much larger improvements given by the C<sub>13</sub>/C<sub>14</sub> alcohol ethoxylate surfactants, 'Marlipal' 34/6EO, 34/11EO, 34/20EO, where 100% control was obtained even at an application rate of 25 g AI ha<sup>-1</sup>. These surfactants had therefore brought about a significant improvement in the performance of the dimethomorph EC formulation.

The WP formulation, in the absence of adjuvants, gave no observable measure of therapeutic control of the disease at any application rate up to 400 g AI ha<sup>-1</sup> (Table 1(b)). However, intermediate levels of control were observed with the addition of either 'Atplus' 412 or 'Atplus' 411F with the levels marginally, but not statistically, below those observed with the EC formulation plus these oils. However the extents of control with the three 'Marlipal' surfactants were equal or greater than 95% at all the application rates of dimethomorph employed and were not significantly different from the EC + 'Marlipal' surfactants in this trial. It was therefore

clear that these adjuvants possessed the ability to change a solid WP formulation from being inactive in therapeutic control of *P. viticola* on vines to one that was highly active and similar in performance to that of a liquid EC formulation + adjuvants.

This was an important observation, because it implied that a good adjuvant system could manipulate the activities of solid formulations of dimethomorph to be better than those of liquid formulations alone and approach those of liquid formulations with adjuvants. That is, the use of an appropriate spray tank adjuvant could reduce any differences in performance between liquid and solid formulations of dimethomorph.

Confirmation of this point was obtained in a second trial examining a range of nonylphenol ethoxylates ('Arkopal' N060, N100, N230), a C<sub>12</sub> alkylamine ethoxylate ('Ethomeen' C12) and a silicone ethoxylate/propoxylate ('Silwet' L77). The results from mixtures with the WP formulation were similar to those from equivalent mixtures with the EC formulation (Tables 2(a), 2(b)) as had been observed with the adjuvants in the first trial. All of the adjuvants in this second trial were highly effective and not statistically different from each other in enhancing the therapeutic fungal activity of dimethomorph.

However, it was observed that plants treated with 'Ethomeen' C12 showed some phytotoxic symptoms of necrotic spots, probably coincident with spray-drop deposits. It is known that some alkylamine ethoxylates

**TABLE 2**  
Effects of Adjuvants on the Therapeutic Control of Two-Day-Old Infections of  
*Plasmopara viticola* on Vine by Dimethomorph Formulations

	Fungal control (%) <sup>b</sup> Dimethomorph application rate, (g ha <sup>-1</sup> )					
Adjuvant type <sup>a</sup>	25	50	100	200	400	Mean <sup>c</sup>
<i>(a) EC formulation</i>						
None	0	16	61	55	68	40
'Arkopal' N060	84	92	<b>97</b>	92	<b>95</b>	92
'Arkopal' N100	84	89	92	89	<b>97</b>	90
'Arkopal' N230	95	<b>95</b>	95	<b>97</b>	<b>97</b>	96
'Ethomeen' C12	<b>100</b>	<b>100</b>	<b>100</b>	<b>97</b>	<b>100</b>	99
'Silwet' L77	92	92	<b>97</b>	<b>100</b>	<b>100</b>	96
<i>(b) WP formulation</i>						
None	0	0	0	0	0	0
'Arkopal' N060	95	95	89	<b>97</b>	97	95
'Arkopal' N100	79	89	71	87	82	82
'Arkopal' N230	<b>97</b>	<b>100</b>	<b>97</b>	<b>97</b>	<b>100</b>	98
'Ethomeen' C12	<b>97</b>	<b>100</b>	<b>97</b>	<b>97</b>	<b>97</b>	98
'Silwet' L77	68	92	92	<b>97</b>	<b>97</b>	89

<sup>a</sup> Adjuvant application rate = 750 g ha<sup>-1</sup>.

<sup>b</sup> Figures in bold type are those identified as not less than 95% control at  $P = 0.05$  by the statistical method.

<sup>c</sup> Mean values of fungal control through the dimethomorph application rate range: these facilitate comparison of the adjuvant treatments.

can cause necrosis and, since phytotoxicity symptoms were not observed with the other adjuvant combinations, but were observed with plants sprayed only with solutions of 'Ethomeen' C12, it seemed reasonable to assume it was an effect of 'Ethomeen' C12 rather than that of increased concentrations of dimethomorph in leaf cellular tissue brought about by the adjuvants.

However, since 'Ethomeen' C12 had brought about a considerable enhancement of dimethomorph performance it seemed appropriate to test a range of alkylamine ethoxylates varying in ethylene oxide content to assess whether the phytotoxicity symptoms could be reduced with different analogues while still maintaining adjuvant-enhanced activity.

The results from testing the 'Genamin' C<sub>12</sub> series of alkylamine ethoxylates confirmed that alkylamine ethoxylates were efficacious adjuvants for dimethomorph (Table 3) and that there was a structure-activity trend in phytotoxicity, decreasing with increase of ethoxylation, as follows:

Genamin code	C020	C050	C100	C200
Phytotoxicity score	5	2.5	1.7	0.7

[visual assessment based on a scale 0–5, 0 = no effect, 1 = small, acceptable effects; 2–4 increasing, unacceptable necrosis, 5 = extensive necrotic patches].

The three lowest ethoxylated analogues, 'Genamin' C020, C050, C100, gave unacceptable levels of phyto-

toxicity. However the highest ethoxylated analogue, 'Genamin' C200, while giving possibly acceptable levels of phytotoxicity, unfortunately produced enhancements of dimethomorph activity lower than with the other analogues and less than that afforded by the best alcohol ethoxylates, 'Genapol' C050, C080, (Table 3). The alkylamine ethoxylates were therefore of no further interest.

The two castor oil ethoxylates ('Emulsogen' EL, EL400 with 36 and 40 moles of ethylene oxide respectively) were insufficiently effective in enhancing dimethomorph activity (Table 3) and so were also of no further interest.

The C<sub>18</sub> tallow oil alcohol ethoxylates ('Genapol' T series) showed a structure-activity pattern with optimum enhancement of dimethomorph activity at an intermediate degree of ethoxylation of ~15 moles, 'Genapol' T150 (Table 3). The higher ethoxylated analogues gave very little enhancement as did the higher ethoxylate member of the two castor oil ethoxylates and it may be that, with these longer aliphatic chain surfactants, their larger molecular volume impedes their diffusion into the leaf cuticle<sup>7–9</sup> and renders them less efficient adjuvants, with a narrower window for optimum ethylene oxide content. The other most active adjuvants, free of serious phytotoxic effects in this trial, were the two C<sub>12</sub> alcohol ethoxylates with 5 and 8 moles of ethylene oxide ('Genapol' C050, C080). These results confirmed the observations made in the first trial

**TABLE 3**  
Effect of Adjuvants on the Therapeutic Control of Two-Day-Old Infections of  
*Plasmopara viticola* on Vine by Dimethomorph EC Formulation

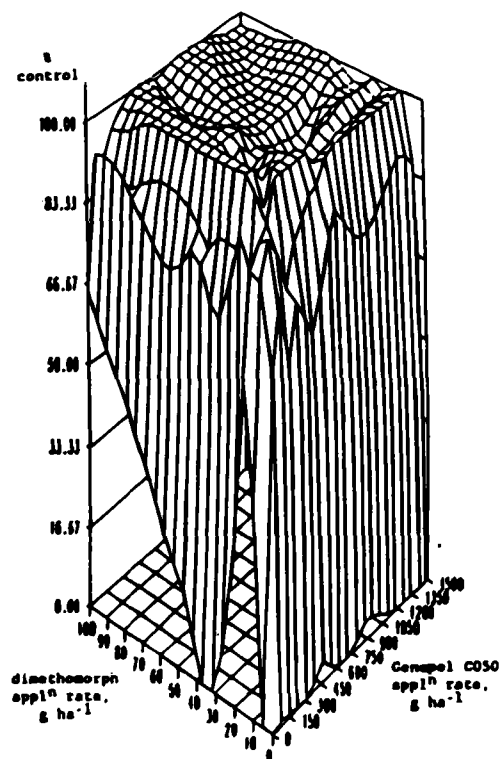
Adjuvant type <sup>a</sup>	Fungal control (%) <sup>b</sup> Dimethomorph application rate (g ha <sup>-1</sup> )				Mean <sup>c</sup>
	6.3	12.5	25	50	
None	0	0	0	0	0
'Genamin' C020	<b>95</b>	<b>99</b>	<b>100</b>	<b>100</b>	99
'Genamin' C050	87	89	91	<b>96</b>	91
'Genamin' C100	58	88	86	88	80
'Genamin' C200	79	76	87	84	82
'Emulsogen' EL	64	52	67	24	52
'Emulsogen' EL400	42	0	31	0	18
'Genapol' T110	76	83	79	89	82
'Genapol' T150	90	<b>97</b>	<b>100</b>	<b>99</b>	97
'Genapol' T250	7	13	0	42	16
'Genapol' T800	0	13	0	38	13
'Genapol' C050	95	93	91	94	93
'Genapol' C080	91	<b>99</b>	<b>97</b>	93	95

<sup>a</sup> Adjuvant application rate = 750 g ha<sup>-1</sup>.

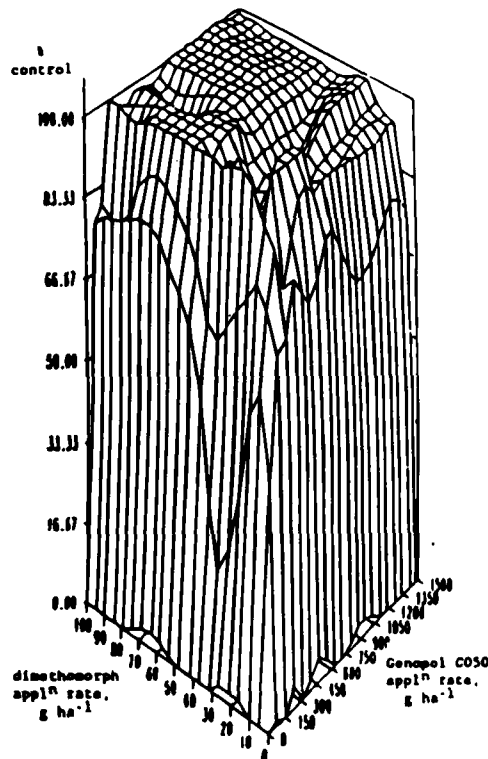
<sup>b</sup> Figures in bold type are those identified as not less than 90% at  $P = 0.05$  by the statistical method II.

<sup>c</sup> Mean values of fungal control through the dimethomorph application rate range which facilitate comparison of the adjuvant treatments.

(a) EC formulation



(b) WP formulation



**Fig. 1** Response surface plots of percentage control of *Plasmopara viticola* on vines at various combinations of 'Genapol' C050 and dimethomorph formulations.

with the C<sub>13</sub>/C<sub>14</sub> 'Marlipal' alcohol ethoxylates and demonstrated that this high adjuvant-enhancement of dimethomorph therapeutic activity was related to the general chemical structure of the adjuvants rather than their specific origins. Alcohol ethoxylates have been observed to be generally efficacious in other recent adjuvant studies with other active ingredients.<sup>10-12</sup>

In reviewing the results with the nonylphenol ethoxylate and silicone ethoxylate surfactants, it was decided to postpone further investigation of these adjuvants at this stage because of possible future restriction of use of alkyl phenol-based surfactants and because of the high cost, without especial benefit, for the silicone ethoxylate. Attention was therefore focused on the alcohol ethoxylates.

In order to determine the likely concentration of these alcohol ethoxylates required for maximum enhancement of dimethomorph activity, a two-dimensional factorial experiment was undertaken in which 'Genapol' C050 and dimethomorph application rates were varied between 0 and 1500 g ha<sup>-1</sup> and 6.3 and 100 g AI ha<sup>-1</sup>, respectively, with both the EC and WP formulations.

As in previous trials, the EC formulation without adjuvant gave some low levels of fungal control but these levels were dramatically increased by even 94 g ha<sup>-1</sup> of 'Genapol' C050 (Table 4). This corresponded to a spray tank concentration of only 0.376 g litre<sup>-1</sup>. These levels of control systematically increased with increase in 'Genapol' C050 application rate as judged by either the dose mean values or the increasing incidence of >90% control at lower application rates of

dimethomorph given in bold type (Table 4). 'Genapol' C050 application rates of 375 g ha<sup>-1</sup> (1.5 g litre<sup>-1</sup>) or higher gave >90% control at three or more of the dimethomorph application rates. From the response surface plot (Figure 1(a)) it can be seen that the optimum combination that gave fungal control, essentially on the plateau of maximum activity, was composed of 25 g ha<sup>-1</sup> dimethomorph and 375 g ha<sup>-1</sup> 'Genapol' C050.

The results with the WP formulation were of the same pattern but with fewer of the combinations giving >90% fungal control (Table 4) and a smaller plateau area for maximum control in the response surface plot (Figure 1(b)) compared with that for the EC formulation (Figure 1(a)). Optimum combinations were either 50 g ha<sup>-1</sup> dimethomorph with 375 g ha<sup>-1</sup> 'Genapol' C050 or 25 g ha<sup>-1</sup> dimethomorph with 750–1500 g ha<sup>-1</sup> 'Genapol' C050 or, of course, intermediate rates of both.

In conclusion, it has been found that alcohol ethoxylates varying in alkyl chain length from C<sub>12</sub> to C<sub>18</sub> and ethylene oxide content between 5 and 20 moles ethylene oxide for the C<sub>12</sub> surfactants and around 15 moles for the C<sub>18</sub> surfactants are effective adjuvants in promoting the therapeutic activity of dimethomorph formulations against *P. viticola* on glasshouse-propagated vines. The fact that there is a broad range of ethylene oxide content of these C<sub>12</sub> alcohol (and nonylphenol) ethoxylate surfactants that achieve high enhancement of dimethomorph activity is in complete accord with recent observations that for neutral compounds of intermediate lipophilicity (log K<sub>ow</sub> = 1–3; dimethomorph log

TABLE 4  
Effect of Genapol C050 Application Rate on the Therapeutic Control of Two-Day-Old Infections of *Plasmopara viticola* on Vine by Dimethomorph Formulations

'Genapol' C050 application rate (g ha <sup>-1</sup> )	Fungal control (%) <sup>a</sup> Dimethomorph application rate (g ha <sup>-1</sup> )					Mean
	6.3	12.5	25	50	100	
(a) EC formulation						
0	0	58	12	19	65	31
94	81	88	91	88	95	89
187	81	91	93	<b>95</b>	88	90
375	84	93	<b>95</b>	<b>100</b>	<b>100</b>	94
750	<b>98</b>	<b>98</b>	<b>98</b>	<b>95</b>	<b>100</b>	98
1500	<b>95</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>98</b>	99
(b) WP formulation						
0	0	0	0	0	0	0
94	57	70	37	78	85	65
187	78	83	89	89	85	85
375	89	94	87	<b>98</b>	<b>96</b>	93
750	91	91	91	<b>98</b>	<b>98</b>	94
1500	85	94	<b>98</b>	<b>98</b>	<b>98</b>	95

<sup>a</sup> Figures in bold type are those identified as not less than 90% control at  $P = 0.05$  by the statistical method II.

$K_{ow} = 2.7$ ) the requirements on ethylene oxide content for maximum foliar penetration is also broad for alcohol ethoxylates with lipophilic moieties in the  $C_{12}$  to  $C_{14}$  range.<sup>12</sup>

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### REFERENCES

1. Albert, G., Curtze, J. & Drandarevski, C. A., Dimethomorph (CME 151), a novel curative fungicide. *Brighton Crop Prot. Conf.—Pests and Diseases*, 1 (1988) 17–24.
2. Laffranque, J. P., Pollet, N. & Garforth, B., Mildew control with dimethomorph. *Phytoma*, **448** (1993) 49–51.
3. Wicks, T. J. & Hall, B., Efficacy of dimethomorph (CME 151) against downy mildew of grapevines. *Plant Dis.*, **74** (1990) 114–16.
4. Wicks, T. J., Hall, B. & Pezsaniti, P., Fungicidal control of downy mildew *Bremia-Lactucae* on lettuce. *Austral J. Exp. Agric.*, **33** (1993) 381–4.
5. Golyshin, N. M., Maslova, A. A. & Goncharova, T. F., A new systemic fungicide against peronosporosis. *Zashchita Rastenii (Moskva)*, (1992) (No. 12), 13.
6. Grayson, B. T., Pack, S. E., Edwards, D. & Webb, J. D., Assessment of a mathematical model to predict spray deposition under laboratory track spraying conditions, II. Examination with further plant species and diluted formulations. *Pestic. Sci.*, **37** (1993) 133–40.
7. Bauer, H. & Schönherr, J., Determination of mobilities of organic compounds in plant cuticles and correlation with molar volumes. *Pestic. Sci.*, **55** (1992) 1–11.
8. Schönherr, J., Effects of monodisperse alcohol ethoxylates on mobility of 2,4-D in isolated plant cuticles. *Pestic. Sci.*, **34** (1993) 155–64.
9. Chaumat, E., Chamel, A., Taillandier, G. & Tissut, M., Quantitative relationships between structure and penetration of phenylurea herbicides through isolated plant cuticles. *Chemosphere*, **24** (1992) 189–200.
10. Holloway, P. J., Stock, D., Whitehouse, P. & Grayson, B. T., Rational approaches to selection of surfactants for optimising uptake of foliage-applied agrochemicals. *Brighton Crop Prot. Conf.—Weeds*, **3** (1989) 225–30.
11. Stock, D., Edgerton, B. M., Gaskin, R. E. & Holloway, P. J., Surfactant-enhanced uptake of some organic compounds: Interactions with two model polyoxyethylene aliphatic alcohols. *Pestic. Sci.*, **34** (1992) 233–42.
12. Stock, D., Holloway, P. J., Grayson, B. T. & Whitehouse, P., Development of a predictive uptake model to rationalise selection of polyoxyethylene surfactant adjuvants for foliage-applied agrochemicals. *Pestic. Sci.*, **37** (1993) 233–45.